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# *Natural Reduction of Graphene Oxide to Graphene using Kaffir Lime Leaves Extract*

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***Abstract*—Previous research has proven that the reduction of graphene from graphene oxide successful via chemical reduction method with hydrazine and dextran; thermal reduction and also vitamin C. In this paper, the natural reduction of graphene from graphene oxide is presented by means of natural reduction to obtain higher reduction rate. The graphene was prepared via modified Hummer's method due to its ability to produce graphene in large quantity. Graphite oxidizes to produce graphite oxide, then synthesizes to graphene oxide. Then, graphene oxide is reduced through natural reduction by using kaffir lime leaves extract. Optimization of the reductant (Kaffir Lime Extract) to produce highest reduction rate was done through the use of a parameter of retention time and concentration. The effectiveness of the reduction process was verified by Ultraviolet-visible spectroscopy (UV-Vis) and the morphology of reduced graphene oxide was identified by using SEM (Scanning Electron Microscope).**

***Keywords—Graphene, graphene oxide,kaffir lime leaves natural reduction***

## I. INTRODUCTION

Chemical reaction is the electron transferring process from an atom to another atom. Graphene from graphene oxide reduction using natural reduction method by kaffir lime leaves has recently been considered as a best choice to substitute existing reducing agents such as hydrazine.[1] Reducing graphene oxide using hydrazine as a reducing agent showed that carbonyl groups binded to the graphene oxide are preserved.[2] Besides that, it was discovered that the reduction of graphene from graphene oxide can be prepared by using dextran as a multifunctional reducing agent.[3]

Current reduction of graphene from graphene oxide can be done by micro-mechanical exfoliation which is a high ordered pyrolytic graphite[4], chemical vapour deposition (CVD) and epitaxial growth[5]. Reference [6] was investigating the use of chemical reagent in the reduction process being very critical for graphene oxide reduction. These clearly shows that there are disadvantages when using chemical reagent because natural response of graphene to detect analyte may be buried by the signals caused by impurities[7]. For example, reduction using hydrazine in large-scale reduction is not desirable because it is highly toxic. Using kaffir lime leaves for reduction contains high concentration of chlorophyll as reducing agent and it can be removed easily during the separation process without the need of modification. The advantages of natural reduction includes the material being readily available and the high potential for commercial use because it is economical.

There are several sources of chlorophyll suitable for reduction of graphene oxide to graphene such as leaves. The reducing method by ethanolic extract of M. oleifera was also used[8]. Using vegetables for natural reduction are not suitable because they can be consumed as food which is more important as compare to using food to produce secondary product. This opens a new opportunity of natural reduction of graphene oxide by using leaves from kaffir lime trees. Growers produces more than 800 tons of kaffir lime leaves annually and this study utilizes these leaves for the reduction of graphene oxide. The kaffir lime leaves have an aroma identified as (–)-(S)-citronellal, which is present in the leaf oil (>80%), small components included citronellol (10%), nerol and lomonene. The small amount of citronellol can also be use as a reducing agent which is acidic in nature and can contribute in the reduction process of graphene oxide. Kaffir lime leaves are cheap and are an abundance in Malaysia, Thailand, Vietnam and Indonesia. Hence this research aims to fully utilize kaffir lime leaves. Due to the high presence of chlorophyll content and are being supported by Citronellol, it has great potential for use as a reducing agent in the reduction process. Industries that require reduction process can consider using kaffir lime leaves as a reducing agent as it is an economical method. Since it is unknown whether the industry that requires the reduction process will benefit positively or negatively, it is also included as an objective of this study.

## II. MATERIALS AND METHODOLOGY

### *A. Materials*

Chemicals were mostly obtained from Sigma Aldriech (concentrated sulfuric acid, concentrated hydrochloric acid, citric acid, potassium persulfate, phophorus pentoxide, potassium permanganate and graphite powder. The kaffir lime

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leaves were obtained in a local supermarket. Some of the common chemicals such as acetone and hydrogen peroxides were obtained from UMP FKKSA chemical warehouse.

### *B. Graphene oxide (GO) synthesis*

The graphene oxide was prepared via modified Hummer's method[9][10]. A solution concentrated sulphuric acid ($H_2SO_4$), potassium persulfate ($K_2S_2O_8$) and phosphorus pentoxide ($P_2O_5$) were prepared and heated at a temperature up to 80°C. 20 grams of graphite powder was then added into the solution and continuously stirred for about 30 minutes. A dark blue mixture was observed. The solution was then cooled at room temperature for 6 hours. This was followed by the addition of deionize water (DI water) to filter and wash the filtrate until it became neutral pH. The filtrate was then be dried overnight at room temperature using a vacuum desiccator. The 20 grams of dried graphite powder was poured into a solution of 0°C concentrated $H_2SO_4$ by using a 2 litre conical flask. 60 grams of potassium permanganate ($KMnO_4$) was then added slowly into the solution through stirring and maintained at temperature below 20°C. Then, the mixture was heated up to 35°C for 2 hours using an oil bath. Effervescent and brownish grey paste formed. Next, 920 mL of DI water was added into the mixture. The temperature was maintained at 98°C for 15 minutes. Another 2.8 litre of DI water and 30% hydrogen peroxide ($H_2O_2$) were added into the mixture. The colour of the mixture changed to bright yellow. The mixture was then filtered with 5 litre of 1:10 concentrated HCl. The cake was dried overnight at room temperature using a vacuum desiccator.

### *C. Verification of Graphene Oxide*

The dry Graphene Oxide synthesized by conventional method was verified by dispersing 0.1 grams of GO into a 50 mL DI water. The mixture was then ultrasonicated for 30 minute. After that, the solution was centrifuged under 10000g for 10 minutes to remove the unexfoliated materials. The supernatant, which is the top layer, is the graphene oxide. Then, the supernatant was measured using UV-Vis Spectrometer by wavelength of 232 nm which is the wavelength of graphene oxide to verify if the synthesis process was completed.

### *D. Preparation of Kaffir Lime Leaves Extract*

Preparation of kaffir lime extract was done by using 250g kaffir lime leaves and blended with 1L of water in a commercial blender. After that, the blended solution was filtered using a vacuum pump. 100ml of the kaffir lime leaves extract was diluted with 900ml of water to make another concentration which is 10 times dilute from the original concentration. The kaffir lime leaves extract was then stored in refrigerator at temperature 3-8ºC.

### *E. Reduction of GO to Graphene*

The reduction was done by dispersing 0.1 grams of GO into a 50 mL DI water. The mixture was then ultrasonicated for 30 minute. After that, the solution was centrifuged under 10000g for 10 mins to remove the unexfoliated materials. The supernatant, which is the top layer, is the graphene oxide. The supernatant graphene oxide was poured into a round bottom flask and the pH of the solution is adjusted to 10 using 5M of potassium hydroxide (KOH).For the next step, the concentrate kaffir lime leaves extract was place under UV light supply and constantly stirred for 30 minutes. The concentration of graphene was measured by using UV-Vis Spectroscopy to measure the absorbancy.

### *F. Optimization of Reduction Period and the Concentration*

In this experiment, the effects of the kaffir lime leaves extract concentration on reduction process were studied with time constant and also monitored with the kaffir lime leaves extract concentration constant. This is important in order to know the optimal amount of reducing agent required with minimal time for the reduction completion. Several parameters were set for the optimizing process as shown in table below:

TABLE 1. OPTIMIZATION PARAMETER AND METHOD OF NATURAL REDUCTION

| Optimization Parameter | Retention time for reduction completion (h) |
|---|---|
| ***Reduction with Concentrate Kaffir Lime Leaves Extract (250g/L)*** | 0 |
| | 3 |
| | 6 |
| | 9 |
| | 15 |
| | 24 |
| ***Reduction with Dilute Kaffir Lime Leaves Extract (25g/L)*** | 0 |
| | 3 |
| | 6 |
| | 9 |
| | 15 |
| | 24 |

## III. RESULT AND DISCUSSION

Synthesis of graphene oxide from graphite powder was successful using conventional method. Dark blue mixture was observed after pre-oxidation process of graphite. Graphite oxide was obtained after oxidation of graphite, brownish grey paste was obtained. Graphene oxide was obtain when the synthesis process was completed and light yellow color paste was observed. The wavelength of graphene oxide (232nm) was verified by UV-Vis Spectrometer and shown the synthesis process was completed.

For natural reduction, the peak obtained from the UV-Vis spectrometry shifted from 232 nm to 273 nm after reduction process. The peak shift confirmed that the reduction of graphene oxide to graphene was complete (Choi et al., 2010). The result of optimization of reduction process was shown in table below:

TABLE 2. UV-VIS SPECTROMETER RESULTS

| Concentration | Time | UV-Vis Reading (273nm) |
|---|---|---|
| 250g/L | 3 | 3.301 |
| | 6 | 3.697 |
| | 9 | 3.780 |
| | 15 | 3.780 |
| | 24 | 3.350 |
| 25g/L | 3 | 3.022 |

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| | | |
|---|---|---|
| | 6 | 3.698 |
| | 9 | 3.750 |
| | 15 | 3.750 |
| | 24 | 3.311 |

High graphene concentration was detected after 3 hours of reduction time and the highest concentration of graphene produce was between 9 to 15 hours reduction time. The concentration of graphene will decrease if the reduction time is more the 15 hours. The concentration of the Kaffir Lime Leaves Extract are not affected by the performance of reduction when using concentrated Kaffir Lime Leaves Extract. Graph 1 show the relationship between Abs(%) in 273nm to dutation of reduction (hour) with different kaffir lime leaves extract concentration (g/L).

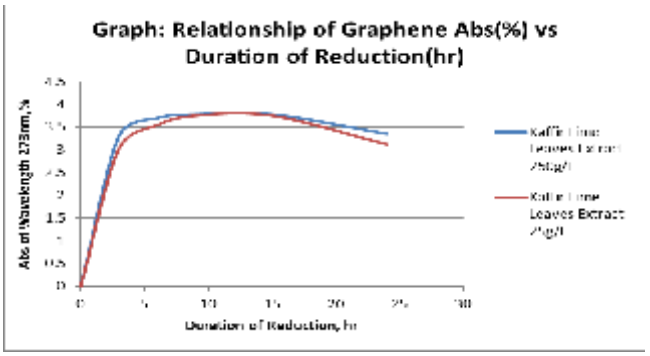


Fig. 1. The Relationship Between Abs(%) in 273nm to Duration of Reduction(hr) with Different Kaffir Lime Extract Concentration(g/L)

## IV. Conclusion

Graphene Oxide can be synthesized by using conventional method from graphite powder. Natural reduction of Graphene Oxide to Graphene was successful by using kaffir lime leaves extract. The duration of reduction time to get high concentration of graphene is a minimum of 3 hours while the highest graphene concentration produced was shown between 9 to 15 hours. The concentration of the kaffir lime leaves will affect the efficiency of reduction process but there is not much difference when using concentrated kaffir lime extract.

The natural reduction process using kaffir lime leaves was recommended to use more dilute reductant factor of 0.01, 0.001 or even more diluted to obtain the minimum concentration requirement for natural reduction process..

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